

FORM PTO-1390 (Modified)  
(REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES**  
**DESIGNATED/ELECTED OFFICE (DO/EO/US)**  
**CONCERNING A FILING UNDER 35 U.S.C. 371**

JMYT-244US

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

To Be Assigned

09/857386

INTERNATIONAL APPLICATION NO.

PCT/GB99/03971

INTERNATIONAL FILING DATE

29 November 1999 (29.11.99)

PRIORITY DATE CLAIMED

05 December 1998 (05.12.98)

TITLE OF INVENTION

**IMPROVEMENTS IN PARTICULATE CONTROL**

APPLICANT(S) FOR DO/EO/US

**PHILLIPS, Paul Richard****TWIGG, Martyn Vincent**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). (UNEXECUTED)
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☐ Other items or information:

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <b>09/857386</b> To Be Assigned	INTERNATIONAL APPLICATION NO. <b>PCT/GB99/03971</b>	ATTORNEY'S DOCKET NUMBER <b>JMYT-244US</b>
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21. The following fees are submitted:				<b>CALCULATIONS PTO USE ONLY</b>	
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b>					
<input type="checkbox"/>	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . .	<b>\$970.00</b>			
<input checked="" type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . .	<b>\$840.00</b>			
<input type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . .	<b>\$690.00</b>			
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . .	<b>\$670.00</b>			
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . .	<b>\$96.00</b>			
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>\$860.00</b>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<b>\$0.00</b>	
<b>CLAIMS</b>	<b>NUMBER FILED</b>	<b>NUMBER EXTRA</b>	<b>RATE</b>		
Total claims	25 - 20 =	5	x \$18.00	<b>\$90.00</b>	
Independent claims	2 - 3 =	0	x \$80.00	<b>\$0.00</b>	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$950.00</b>	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$950.00</b>	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$950.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$950.00</b>	
				<b>Amount to be refunded</b>	<b>\$</b>
				<b>charged</b>	<b>\$</b>

- ☒ A check in the amount of **\$950.00** to cover the above fees is enclosed.
- ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **18-0350** A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

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**Christopher R. Lewis**

NAME

**36,201**

REGISTRATION NUMBER

**June 5, 2001**

DATE

JMYT-244US

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Paul Richard Phillips et al. : Art Unit:  
 Application No.: To Be Assigned : Examiner:  
 Filed: Herewith :  
 FOR: IMPROVEMENTS IN PARTICULATE :  
 CONTROL

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
 Washington, DC 20231

SIR:

Prior to examination, please amend the above-identified application as follows.

IN THE CLAIMS:

Please replace claims 1, 3, 6, 8, 9, 11-14, 16, and 19, with the following amended claims:

- 1                   1.     (Amended) A process of treating internal combustion  
 2     engine exhaust gas containing O<sub>2</sub>, NO<sub>x</sub>, unburnt hydrocarbon ("HC"), CO  
 3     and soot, comprising:
  - 4                   i.     oxidising a substantial part of the HC;
  - 5                   ii.    treating the product of step i to oxidise NO to NO<sub>2</sub>;
  - 6                   iii.   collecting soot; and
  - 7                   iv.    combusting the collected soot by reaction with the NO<sub>2</sub>  
 8                   and possibly any O<sub>2</sub> left over after steps i and ii.
- 1                   3.     (Amended) Process according to claim 1 carried out  
 2     over:

3                   i.       a first catalyst adapted to be fed with engine exhaust gas  
4 and effective to promote oxidation of HC therein;

5                   ii.     a second catalyst adapted to be fed with the product of i  
6 and effective to promote oxidation of NO to NO<sub>2</sub>;

7                   iii.    a filter effective to collect soot and to retain it until  
8 combusted by said NO<sub>2</sub> and any O<sub>2</sub> left over after catalyst i and ii.

1                   6.     (Amended) Process according to claim 1, wherein the  
2 HC is in gaseous form.

1                   8.     (Amended) Process according to claim 6 in which the  
2 gas leaving step/catalyst i undergoes cooling and then enters step/catalyst ii.

1                   9.     (Amended) Process according to claim 6, further  
2 comprising providing an increased amount of combustible upstream of a first  
3 catalyst for effecting step i for increasing the temperature at which step i  
4 operates.

1                   11.    (Amended) Process according to claim 6 in which a first  
2 catalyst for effecting step i has a very low light-off temperature for HC and  
3 CO oxidation.

1                   12.    (Amended) A process according to claim 1, wherein the  
2 HC is absorbed on the soot.

1                   13.    (Amended) Process according to claim 1 further  
2 comprising removing NO<sub>x</sub> downstream of soot combustion.

1                   14.    (Amended) Process according to claim 13 wherein  
2 removing NO<sub>x</sub> uses a regenerable NO<sub>x</sub> absorber downstream of the  
3 collecting trap.

1                   16.    (Amended) System for treating internal combustion  
2 engine gas containing O<sub>2</sub>, NO<sub>x</sub>, unburnt hydrocarbon ("HC"), CO and soot,  
3 comprising:

- 4 i. a first catalyst to receive engine exhaust and effective to  
5 promote oxidation of HC therein;
- 6 ii. a second catalyst receiving the product of the first  
7 catalyst and effective to promote oxidation of NO to  
8 NO<sub>2</sub>; and
- 9 iii. a filter effective to collect soot and to retain it until  
10 combusted by reaction with said NO<sub>2</sub> and, depending on  
11 conditions, any O<sub>2</sub> left over after the first catalyst.

1 19. (Amended) A diesel engine in combination with a  
2 system according to claim 16 connected to its exhaust.

Please add the following new claim:

1 25. (Newly Added) Process according to claim 1 wherein  
2 step i further comprises oxidising some NO to NO<sub>2</sub>.

Respectfully submitted,



Christopher R. Lewis, Reg. No. 36,201  
Attorney for Applicants

CRL/lrb

Dated: June 5, 2001

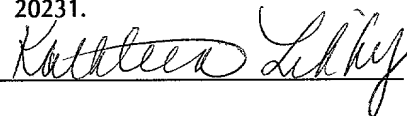
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The Assistant Commissioner for Patents is  
hereby authorized to charge payment to  
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I hereby certify that this paper and fee are being  
deposited, under 37 C.F.R. § 1.10 and with sufficient  
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Washington, D.C. 20231.

Kathleen Libby



**VERSION WITH MARKINGS TO SHOW CHANGES MADE****IN THE CLAIMS:**

- 1                   1.     (Amended) A process of treating internal combustion  
2 engine exhaust gas containing O<sub>2</sub>, NO<sub>x</sub>, unburnt hydrocarbon ("HC"), CO  
3 and soot, comprising:
- 4                   i.     oxidising a substantial part of the HC, ~~with possibly~~  
5 ~~some oxidation of NO to NO<sub>2</sub>~~;
- 6                   ii.    treating the product of step i to oxidise NO to NO<sub>2</sub>;
- 7                   iii.   collecting soot; and
- 8                   iv.    combusting the collected soot by reaction with the NO<sub>2</sub>  
9 and possibly any O<sub>2</sub> left over after steps i and ii.
- 1                   3.     (Amended) Process according to claim 1 ~~or claim 2~~  
2 carried out over:
- 3                   i.     a first catalyst adapted to be fed with engine exhaust gas  
4 and effective to promote oxidation of HC therein;
- 5                   ii.    a second catalyst adapted to be fed with the product of i  
6 and effective to promote oxidation of NO to NO<sub>2</sub>;
- 7                   iii.   a filter effective to collect soot and to retain it until  
8 combusted by said NO<sub>2</sub> and any O<sub>2</sub> left over after catalyst i and ii.
- 1                   6.     (Amended) Process according to ~~any one of the~~  
2 ~~preceding claims~~ claim 1, wherein the HC is in gaseous form.
- 1                   8.     (Amended) Process according to claim 6 ~~or claim 7~~ in  
2 which the gas leaving step/catalyst i undergoes cooling and then enters  
3 step/catalyst ii.

1           9.     (Amended) Process according to ~~any one of the claims~~  
2 ~~6, 7, and 8, including the provision of~~ claim 6, further comprising providing  
3 an increased amount of combustible upstream of the step a first catalyst for  
4 effecting step i, whereby to increase for increasing the temperature at which  
5 ~~that step i~~ operates.

1           11.    (Amended) Process according to ~~any one of the claims 6~~  
2 ~~to 10~~ claim 6 in which ~~the~~ a first catalyst for effecting step i has a very low  
3 light-off temperature for HC and CO oxidation.

1           12.    (Amended) A process according to ~~any one of claims 1~~  
2 ~~to 5~~ claim 1, wherein the HC is absorbed on the soot.

1           13.    (Amended) Process according to ~~any one of the~~  
2 ~~preceding claims including also~~ claim 1 further comprising removing NOx-  
3 ~~removal~~ downstream of soot combustion.

1           14.    (Amended) Process according to claim 13 ~~including also~~  
2 wherein removing NOx uses a regenerable NOx absorber downstream of the  
3 collecting trap.

1           16.    (Amended) System for ~~carrying out a process according~~  
2 ~~to any one of the preceding claims~~ treating internal combustion engine gas  
3 containing O<sub>2</sub>, NOx, unburnt hydrocarbon ("HC"), CO and soot,  
4 comprising:

5           i.     a first catalyst to receive engine exhaust and effective to  
6 promote oxidation of HC therein;

7           ii.    a second catalyst receiving the product of the first  
8 catalyst and effective to promote oxidation of NO to  
9 NO<sub>2</sub>; and

10          iii.   a filter effective to collect soot and to retain it until  
11 combusted by reaction with said NO<sub>2</sub> and, depending on  
12 conditions, any O<sub>2</sub> left over after the first catalyst.

- 1                   19. (Amended) A diesel engine in combination with a  
2 system according to ~~any one of the claims 16 to 18~~ claim 16 connected to its  
3 exhaust.

Claim 25 has been added.



IMPROVEMENTS IN PARTICULATE CONTROL

- 5       The invention concerns improvements in emissions control, especially from internal combustion engines such as diesel and other lean-burn engines.

Lean-burn engines present problems in that it is difficult to reduce NO<sub>x</sub> emissions in the presence of oxygen. Compression ignition ("diesel") engines and some types of  
10   gasoline engines emit combustible particulate ('soot'). Although engine design, fuelling strategies and devices such as exhaust gas recirculation can decrease engine-out, NO<sub>x</sub> levels, it remains difficult to decrease both NO<sub>x</sub> and soot to below modern limits, such as are expected to be prescribed in European Stage IV regulations.

- 15       The difficulty appears to be greater for low exhaust gas temperatures, for example resulting from engine design such as light duty turbo-charged direct injection diesel engines, especially if fitted with EGR, or from light duty generally.

However, there are a great many naturally aspirated diesel engines used throughout  
20   the world in vehicles, maritime craft and in stationary power sources. Although many modern engine designs utilise turbo-charging, there is a huge population of naturally aspirated engines, and this will be the case for the foreseeable future. Also, it is to be noted that in some countries, including particularly Japan, the performance enhancements from turbo-charging are not adjudged to be worthwhile, and indeed for  
25   some markets, turbo-chargers are removed from modern engines during truck or bus building or re-building. All diesel engines generate soot, but the soot from naturally aspirated engines is "wet" soot, that is it carries a considerable proportion of hydrocarbons absorbed into the particles. There are currently health concerns about the types of hydrocarbons absorbed on the soot. Although the present invention in another  
30   aspect has particular application to naturally aspirated diesel (compression ignition) engines, it may also find application in other engine designs which generate such particulates.

- One particularly effective treatment for diesel exhaust is that marketed by  
35   Johnson Matthey PLC as the "Continuously Regenerating Trap" ("CRT" -RTM). In the

CRT system as disclosed in EP-A-0341832 an oxidation catalyst converts NO in the exhaust to NO<sub>2</sub>, the gas enriched with NO<sub>2</sub> is passed into a filter for the soot and the NO<sub>2</sub> causes facile combustion of the soot, thus continuously regenerating the filter and preventing blocking. The CRT is especially suited to so-called heavy-duty diesel engines as used in buses and larger trucks, where exhaust gas temperatures are generally relatively high.

In the case of turbo-charged direct injection engines used in light duty applications such as cars and light trucks, the exhaust gases are relatively cool, which with other factors makes the CRT system rather less effective than with heavy duty engines.

The invention provides a process of treating internal combustion engine exhaust gas containing O<sub>2</sub>, NO<sub>x</sub>, unburnt hydrocarbon ("HC"), CO and soot, comprising:

- i. oxidising a substantial part of the HC, with possibly some oxidation of NO to NO<sub>2</sub>;
- ii. treating the product of step i to oxidise NO to NO<sub>2</sub>;
- iii. collecting soot; and
- iv. combusting the collected soot by reaction with the NO<sub>2</sub> and possibly any O<sub>2</sub> left over after steps i and ii.

The invention also provides a system for treating such internal combustion engine exhaust gas, comprising:

a first catalyst to receive engine exhaust gas and effective to promote oxidation of *inter alia* HC therein;

a second catalyst receiving the product of the first catalyst and effective to promote oxidation of NO to NO<sub>2</sub>;

a filter effective to collect soot and retain it until combusted by said NO<sub>2</sub> and possibly any O<sub>2</sub> left over after the first and second catalyst.

Since the gas contains soot, the first and second catalysts are suitably supported on a structure permitting passage of fine solid particles. The structure preferably provides through passages, for example in a honeycomb having at least 50, possibly more, the range 100-900 cells/inch<sup>2</sup> being generally preferred, more preferably 100 to 400 cells/in<sup>2</sup>.

The honeycomb may be composed structurally of ceramic or metal. Such ceramic may be for example alumina, silica, titania, zirconia or combinations such as example cordierite or silicon carbide. Such metal may be for example a refractory steel for example Fecralloy. Such metal may make it practicable to provide more passages per square inch, eg up to 1200. Alternative monolithic supports are available, and it is intended to include static fluid mixers and the like, as required and subject to routine testing.

The support structure carries a coating ('washcoat') of high-surface support material for catalytically active components. For the first catalyst the coating and these components are chosen so that it is effective to remove substantially all the HC. (It will normally also effect oxidation of CO to CO<sub>2</sub> and, to some extent, of NO to NO<sub>2</sub>). We believe, although we do not wish to be confined to such belief, that removing gaseous HC before oxidising NO to NO<sub>2</sub> removes species inhibiting such NO oxidation. Although part of the NO may be converted to NO<sub>2</sub> over the first catalyst, unconverted NO is more effectively converted over the second catalyst. In the second embodiment of the present invention, HC absorbed on "wet" soot is combusted over the first catalyst.

An effect of the first catalyst can be to increase the temperature at the inlet of the second catalyst to a level at which the velocity of NO to NO<sub>2</sub> conversion is sufficient to provide more NO<sub>2</sub>: the subsequent soot combustion reactions are also then faster. The resulting temperature should not of course be in a range at which NO<sub>2</sub> formation is equilibrium limited.

In the first embodiment of the invention, it is desirable to obtain an adequate reaction rate over the first catalyst for the reaction of gaseous HC; its inlet temperature is preferably maximised by disposing that catalyst as close as possible to the engine outlet. Thus it is typically mounted in the cylinder block region, for example on the exhaust gas manifold before or after a turbo-charger if used. To attain or increase such temperature rise, additional fuel eg diesel fuel, may be dosed upstream of the first catalyst and oxidised thereon. Alternatively or additionally, the engine inlet fuel injection profile may be adjusted to increase the HC, or more conveniently the CO, content of the raw exhaust gas. Preferably such measures to increase gas temperature continue to provide a lean gas composition. Enrichment with HC and/or CO may be continuous or, preferably,

intermittent and initiated upon the detection of appropriate exhaust gas conditions. However attained, the temperature at the outlet of the first catalyst stage is preferably at least 200°, and eg up to 500°C.

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Preferably the first catalyst has a very low light-off temperature for both the CO and HC oxidation reactions. This is an additional benefit during parts of the engine operating cycle in which exhaust gas temperatures are temporarily low, eg during idle.

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In the second embodiment, the first catalyst contains a component capable of oxidising hydrocarbons of the type absorbed on wet soot. Suitable forms of ceria are particularly indicated, and such catalysts may comprise other components, as well as preferably one or more platinum group metal catalyst dispersed on an oxide support, which in turn is desirably carried on a monolithic catalyst support.

15

A particularly preferred first catalyst for the second embodiment comprises platinum dispersed on ceria, or on a metal oxide washcoat which incorporates ceria. The platinum loading may be up to 200g/cuft. Other catalytic or promoting elements may also be present. The ceria may be present as a washcoat over a platinum-catalysed alumina or over another catalyst.

20

Whereas the second catalyst may have the same composition as the first, it is suitably designed to be more effective for the NO to NO<sub>2</sub> reaction, and the temperature and/or space velocity, for example, may be different as between the two catalysts. Thus the conditions for the HC oxidation and NO oxidation may be independently optimised. The temperature in the second catalytic step is preferably in the range 150 to 350°C. (Since oxidation of NO is not strongly exothermic, there is little difference between inlet and outlet temperatures).

25

30

In the catalysts the active material comprises generally a platinum group metal ("PGM"), especially platinum and/or palladium, optionally with others eg rhodium. The exact composition of the catalyst is chosen to suit local requirements. Desirably they have relatively high (eg 10-150 g/ft<sup>3</sup>) loadings of platinum, and optionally may have other catalyst components such as rhodium or palladium or catalyst promoter

compounds.

The soot filter may be any capable of collecting the soot without causing excessive back-pressure. Its detailed specification is chosen according to the particular engine characteristics and the regulations to be met. It may be a ceramic wall flow filter, a ceramic foam filter, ceramic fibre filter, sintered metal or wire mesh filter of any suitable type. It may provide for removal of 50 to 100%, preferably at least 60%, more preferably 85%, or greater, of the measured soot in the exhaust gas. There may be a fail-safe bypass or a two-stage filter to cater for a situation where the filter would otherwise be blinded or blocked under certain engine operating conditions. If desired, the filter may be catalysed or part-catalysed to assist combustion. A variety of catalysts are known to be suitable, and these include one or more oxides of vanadium, cerium, and mixed Cs/La/V oxide and supported PGMs. The invention includes the possibility of initiating combustion of the soot if required, for example if the engine operating conditions are such that considerable soot is being/has been generated but the gas temperatures are rather too low for significant combustion; for example initiation may be by providing electric heating of a portion of the filter. The soot is generally carbon and/or heavy hydrocarbons, and is converted to carbon oxides and steam.

It is desirable to use low sulphur-content diesel fuel, suitably below 50ppms, and more preferably "ULSD" or ultra-low sulphur diesel of 10ppms or lower.

The invention provides also an engine in combination with a system as herein defined and a process of operating such an engine.

In this combination, in the first embodiment the first catalyst may be disposed close to the source of exhaust gas, to obtain a maximum convenient operating temperature and reaction rate therein. The outlet gas from that catalyst may undergo cooling, for example in a non-insulated or finned pipe, before entering the second catalyst.

In the combination of the second embodiment, the first catalyst is suitably disposed close to, desirably in, the same housing or "can", as the second catalyst and the filter. It is possible to contemplate a single catalyst monolith or "brick", one end of which carries the first catalyst, and the other end of which carries the second

catalyst, providing appropriate catalyst design and catalyst manufacturing technology is used, and providing that gas flow rates and space velocities are suitable.

5           The combination may include expedients such as EGR.

          The combination may include sensors for at least one of: fuel composition; air/fuel ratio at engine inlet; exhaust gas compositions at critical stages; pressure drop. If engine inlet adjustment and/or fuel injection is used, then a temperature sensor after the  
10   first catalyst, and possibly before that catalyst and/or at the inlet of the NO oxidation catalyst are preferably provided. The control system may include also indicator means informing the engine operator, computer means effective to evaluate the data from the sensor(s), and control linkages effective to adjust the engine to desired operating conditions taking account of eg start-up, varying load and chance fluctuations, and to  
15   inject fuel into the exhaust gas if desired.

          Preferably the engine is a diesel engine, although other engines, including direct injection gasoline engines, may also benefit from the invention. The engine may be the motive power for a vehicle, or may be a stationary power source or auxiliary power  
20   source. Most usefully the first embodiment is applied to a light duty engine as defined above, especially powering a passenger car or light truck or van. Generally "light" means less than 3500kg unladen weight. This may typically correspond to a cylinder capacity up to 6.0 litres and a power output up to 300 KW. The invention is potentially of value for engine for other duties. Desirably, the second embodiment is applied to "heavy duty  
25   diesel" engines.

          It is believed, although we do not wish to be restricted by any theory, that the system and process of preferred embodiments of the invention, whilst permitting combustion of hydrocarbons in the first zone, generates sufficient NO<sub>2</sub> in the second  
30   zone to provide the right balance of NO<sub>2</sub> to carbon for combustion in the particular trap, under typical diesel operating conditions.

          If desired, the present invention may be combined with additional means to reduce NO<sub>x</sub> in the gases leaving the system of the invention, which may include one or

both of NO<sub>x</sub> reduction catalysts, including catalysts of the three-way type or systems incorporating reductant addition and a suitable catalyst, and a regenerable absorber. Such means are generally known.

5

The first embodiment of the invention is illustrated with reference to the accompanying drawings, in which: figure 1 is a schematic drawing of a system according to the invention; figure 2 is a graph comparing the conversions of NO to NO<sub>2</sub> in the presence of HC (prior art) and absence of HC (invention).

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Referring to figure 1, a light-duty turbo-charged direct-injection diesel engine (not shown) discharges its exhaust, containing *inter alia* HC and soot, into a system comprising reactors 10 and 12, connected together for gas flow at region 14. Region 14 is shown by pecked lines to indicate that the connection may be short or may be relatively long, for example with reactor 10 at the engine outlet and reactor 12 under the vehicle body. Such a long connection may itself provide cooling or may include a finned region. Reactor 10 optionally includes at its inlet 16 the sparging spray injector 18. It essentially includes bed 20, of catalyst primarily for oxidation of HC and CO, the HC content of the gas entering bed 20 being HC exhausted by the engine, possibly augmented by HC injected at 18. Control means (not shown) responsive to the temperature of the gas leaving bed 20 regulates engine inlet conditions and HC injection at 18, to keep the temperature of bed 20 high enough for sufficiently rapid HC oxidation.

Reactor 12 contains at its inlet the bed 22 of catalyst primarily for oxidation of NO to NO<sub>2</sub>. The gas leaving bed 22, enriched in NO<sub>2</sub>, passes into soot filter 24, where soot is trapped and oxidised by reaction with the NO<sub>2</sub> and O<sub>2</sub>. Beds 22 and 24 constitute a "CRT" system. The gas, now substantially soot-free, may pass out to atmosphere if air quality regulations permit. Optionally the system may include, in the same reactor or possibly in a separate one, bed 26, charged with NO<sub>x</sub> absorption material, possibly with an injector (not shown) for reductant or ammonia between 24 and 26, and possibly with a catalyst for reduction of NO<sub>x</sub> to N<sub>2</sub>.

Each bed in the system is in the form of a ceramic honeycomb, with (except filter 24) an alumina washcoat carrying active material.

### EXAMPLE 1

A synthetic exhaust gas of the following composition v/v was used:

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CO <sub>2</sub>	4.5 %
H <sub>2</sub> O	4.5 %
O <sub>2</sub>	12.0 %
CO	200 ppm
NO	400 ppm
C <sub>3</sub> H <sub>6</sub>	0 or 400ppm or 800ppm
N <sub>2</sub>	balance.

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This was passed over a 1% w/w platinum on gamma alumina catalyst in particle form in a laboratory reactor at temperatures between 150°C and 500°C. This reactor is known to represent a typical exhaust catalyst consisting of platinum on an alumina washcoat on a honeycomb. The compositions of the outlet gas are shown in figure 2.

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The plots for gas containing 400ppm and 800ppm HC (propylene) show there is very little conversion below about 200°C. However, in the absence of hydrocarbon (as removed in bed 20), already there is 20% conversion at 150°C and 85% conversion at 200°C. It is evident that once the HC (represented by C<sub>3</sub>H<sub>6</sub>) has been removed in the first oxidation step the oxidation of NO to NO<sub>2</sub> can take place more completely, affording more NO<sub>2</sub> for the combustion of particulate in the subsequent step of CRT. Bearing in mind the cool exhaust gas temperatures met with in modern light duty diesel engine designs, the significantly improved conversion at temperatures below 200°C resulting from the removal of gaseous HC, is particularly useful.

### EXAMPLE 2

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The exhaust of a 4 cylinder turbo-charged direct injection Diesel engine of 2.5 litre capacity with EGR and operated at an air-fuel weight ratio of about 30 was fed to the first of 2 catalytic stages of a system as shown in fig 1 of the drawings. The inlet exhaust gas composition v/v was:



	CO <sub>2</sub>	5.0%
	H <sub>2</sub> O	4.9%
	O <sub>2</sub>	13.0%
5	CO	800 ppm
	NO	100 ppm
	N <sub>2</sub>	balance

Catalysts 20 and 22 comprised platinum group metal supported on an alumina-containing washcoat on a 400 cpsi cordierite honeycomb. Catalyst 20 was mounted just outside the engine exhaust manifold after the turbo-charger; catalyst 22 was 1.0m downstream in an underfloor position. For some runs this was adjusted by injection of Diesel fuel using sparger 18, giving a lower but still lean air/fuel ratio. Comparative runs were carried out using at 20 another sample of the same washcoated honeycomb but without catalytic material. Runs were made at a range of load levels, giving temperatures in the range of 225° to 325°C, measured at 22 inlet. The outlet gas was analysed for NO, and total NOx and NO<sub>2</sub> calculated by difference. The table shows the concentration of NO and NO<sub>2</sub> at representative temperatures.

Temp°C		225°		275°		325°	
N oxide		NO	NO <sub>2</sub>	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>
No Fuel	Cat	82	5	78	36	68	63
	Non-cat	96	1	80	18	70	54
+ Fuel	Cat	71	3	73	33	84	42
	Non-cat	65	3	78	26	88	36

It is evident that, except at the lowest temperature in presence of added fuel, the use of the first stage catalyst gives a significantly higher concentration of NO<sub>2</sub>, thus providing for more efficient combustion of collected soot on filter 22.

The second embodiment of the invention is now exemplified below. A variety of

typical oxide catalyst supports, in particulate form, were impregnated with Pt at the wt% shown in Table 1, using aqueous solution of Pt salts, by the incipient wetness technique.

The powdered samples were dried in air at 90°C. All samples were then calcined at  
5 500°C for 3 hours in air.

The samples were impregnated with standard commercial diesel engine lubricating oil at 10wt% per sample, and physically mixed to absorb the oil. Thermo-Gravimetric Analysis and Differential Thermal Analysis was performed on approx 40 mg  
10 samples using a STA 1500 machine using an air atmosphere, at a ramp rate of 10°C/min.

The temperature of onset of combustion was determined, and the area under the DTA peak (expressed on a time basis, and normalised for sample weight) gives a relative measure of the oil combusted versus oil volatilisation. A TGA/DTA plot of a sample of  
15 the lubrication oil showed that volatilised occurred between ca 240 and 400°C, and that combustion occurred above ca. 400°C. The results for ceria and  $\gamma$ -alumina are shown below in Table 1.

Table 1

20	Exp	Sample	Pt-loading (Wt%)	DTA Onset Temp (°C)	DTA
					Peak Area ( $\mu$ V-S/mg sample)
	1	$\gamma$ -alumina	0.0	226	1098
	2	$\gamma$ -alumina	0.25	209	1108
25	3	ceria	0.0	134	2104
	4	ceria	0.009	138	2165
	5	ceria	0.0375	140	2125
	6	ceria	0.25	132	2361

30 It can be seen that both samples of  $\gamma$ -alumina have a relatively high DTA onset temperature, but all samples of ceria show a very significant reduction, into the range of temperatures commonly met with in diesel exhaust gases. All the ceria-based tests illustrate significant combustion of the hydrocarbon oil at low temperatures.

Additional tests were carried out in essentially the same manner, but using mixtures of ceria and platinum catalysed  $\gamma$ -alumina, with one or both of the ceria and alumina impregnated with 10 wt% of oil. The results are shown in Table 2 below:

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Table 2

No.	Sample	Pt( $\text{Al}_2\text{O}_3$ )	DTA Onset	DTA
		Loading (wt%)	Temp ( $^{\circ}\text{C}$ )	Peak Area
10	1 Ceria <sup>OIL</sup> /alumina	0.25	147	1182
	2 Ceria/alumina <sup>OIL</sup>	0.25	159	1147
	3 Ceria <sup>OIL</sup> /alumina <sup>OIL</sup>	0.25	156	1355
	4 (ceria/alumina) <sup>OIL</sup>	0.25	148	1915

15

The beneficial effect of the presence of ceria can be seen in all samples.

CLAIMS

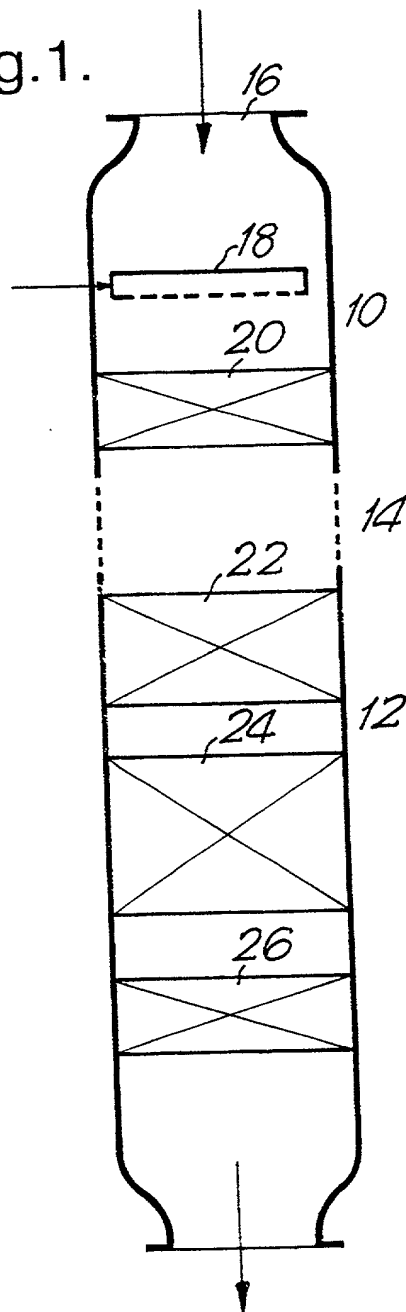
1. A process of treating internal combustion engine exhaust gas containing O<sub>2</sub>, NO<sub>x</sub> unburnt hydrocarbon ("HC"), CO and soot, comprising:
  - 5 i. oxidising a substantial part of the HC, with possibly some oxidation of NO to NO<sub>2</sub>;
  - ii. treating the product of step i to oxidise NO to NO<sub>2</sub>;
  - iii. collecting soot; and
  - iv. combusting the collected soot by reaction with the NO<sub>2</sub> and possibly any O<sub>2</sub> left over after steps i and ii.
- 10 2. Process according to claim 1 in which at least steps i and ii are effected catalytically.
- 15 3. Process according to claim 1 or claim 2 carried out over:
  - i a first catalyst adapted to be fed with engine exhaust gas and effective to promote oxidation of HC therein;
  - ii a second catalyst adapted to be fed with the product of i and effective to promote oxidation of NO to NO<sub>2</sub>;
  - 20 iii a filter effective to collect soot and to retain it until combusted by said NO<sub>2</sub> and any O<sub>2</sub> left over after catalyst i and ii.
4. Process according to claim 3 in which the catalysts are honeycomb-supported.
- 25 5. Process according to claim 4 in which the cell density of the honeycomb is in the range 100-900 per square inch.
6. Process according to any one of the preceding claims, wherein the HC is in gaseous form.
- 30 7. Process according to claim 6 in which the first oxidation is carried out close to the source of exhaust gas, whereby to obtain a maximum convenient operating temperature and reaction rate.

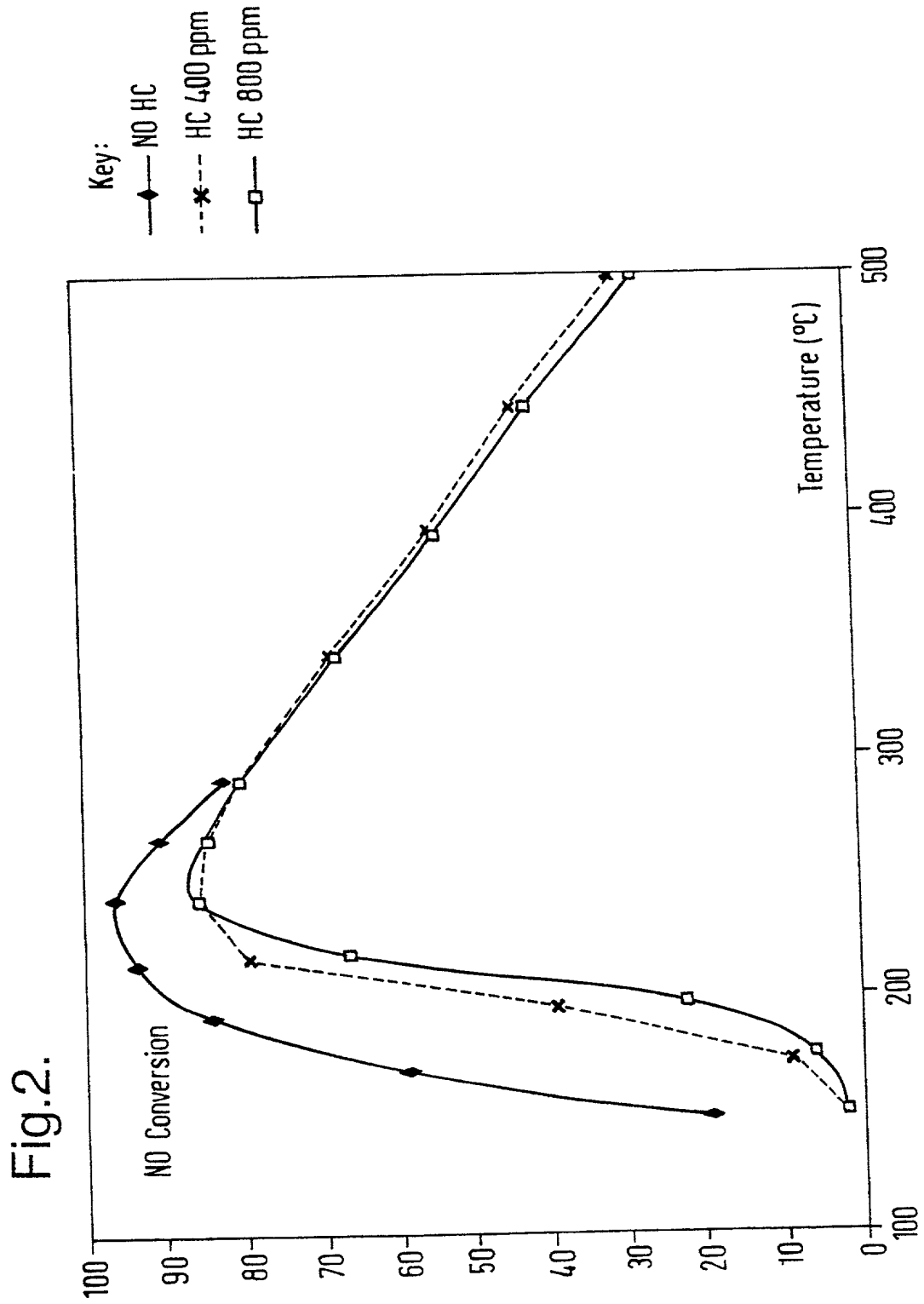
8. Process according to claim 6 or claim 7 in which the gas leaving step/catalyst i undergoes cooling and then enters step/catalyst ii.
- 5 9. Process according to any one of the claims 6,7, and 8, including the provision of combustible upstream of the step catalyst i, whereby to increase the temperature at which that step operates.
- 10 10. Process according to claim 9 in which said combustible is provided by modifying engine settings to pass more HC and/or generate more CO.
11. Process according to any one of the claims 6 to 10 in which the first catalyst has a very low light-off temperature for HC and CO oxidation.
- 15 12. A process according to any one of claims 1 to 5, wherein the HC is absorbed on the soot.
13. Process according to any one of the preceding claims including also NO<sub>x</sub>-removal downstream of soot combustion.
- 20 14. Process according to claim 13 including also a regenerable NO<sub>x</sub> absorber downstream of the collecting trap.
15. Process according to claim 14 including catalytic NO<sub>x</sub>-removal downstream of the NO<sub>x</sub> absorber.
- 25 16. System for carrying out a process according to any one of the preceding claims comprising:
- 30 i. a first catalyst to receive engine exhaust and effective to promote oxidation of HC therein;
- ii. a second catalyst receiving the product of the first catalyst and effective to promote oxidation of NO to NO<sub>2</sub>;
- iii a filter effective to collect soot and to retain it until combusted by reaction with said NO<sub>2</sub> and, depending upon conditions, any O<sub>2</sub> left over after the first

catalyst.

17. System according to claim 16 in which the catalysts are honeycomb-supported.
- 5 18. System according to claim 17 in which the cell density of the honeycomb is in the range 100-900 per square inch.
19. A diesel engine in combination with a system according to any one of claims 16 to 18 connected to its exhaust.
- 10 20. An engine according to claim 19 which is one designed for light duty applications.
21. An engine according to claim 20 which is of the turbo-charged direct injection type.
- 15 22. An engine combination according to claim 19, which is a heavy duty engine.
23. An engine combination according to claim 22, wherein the first catalyst is positioned close to the second catalyst.
- 20 24. An engine combination according to claim 23, wherein the first catalyst and the second catalyst are at opposite ends of a single catalyst monolith.

Fig.1.







# Declaration and Power of Attorney For Patent Application

## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

IMPROVEMENTS IN PARTICULATE CONTROL,

the specification of which is attached hereto unless the following box is checked:



was filed on June 5, 2001 as

United States Application Number or PCT International Application Number 09/857,386

and was amended on June 5, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Not Claimed

9913300.1

Great Britain

June 9, 1999

(Number)

(Country)

(Day/Month/Year Filed)

☐

9826748.7

Great Britain

December 5, 1998

(Number)

(Country)

(Day/Month/Year Filed)

☐

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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